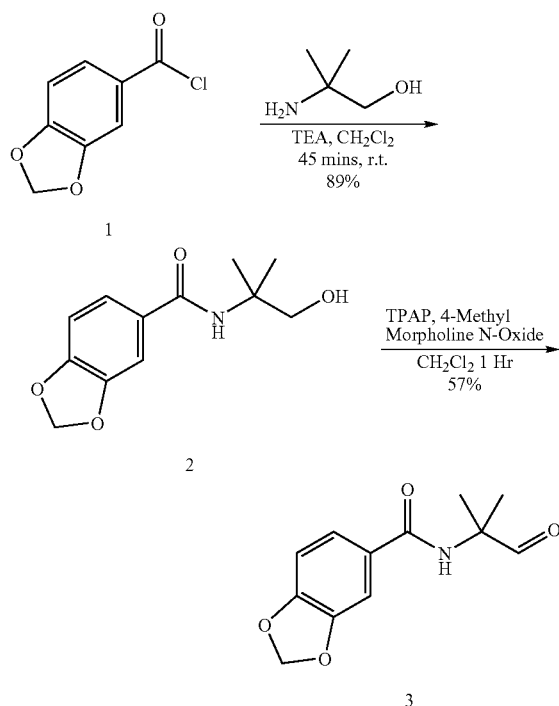


mins. The reflux condenser was replaced with a distillation head and the excess thionyl chloride was distilled from the reaction pot. The oil bath temperature was increased to 120° C. to facilitate distillation. After 2 hours, the reaction vessel was cooled to 23° C. and placed under reduced pressure (~25 Torr). The reaction vessel was then heated to 90° C. for 20 mins, then to 120° C. for 90 minutes to remove any excess remaining thionyl chloride. The reaction vessel was then cooled to 23° C. and then equipped with a clean distillation head and collection flask. The vessel was placed into a 160° C. oil bath and the product was distilled from the reaction pot (b.p.=124° C.@~25 Torr), furnishing 4 as a colorless oil in near quantitative yield.

Example 15

[0511]



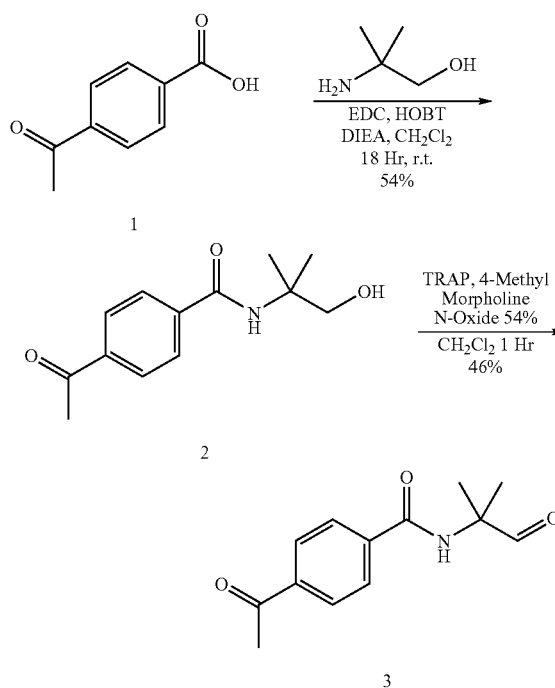
[0512] Piperonyl Chloride (1, 7.8 g, 42 mmol) was added to a solution of 2-amino-2-methyl-1-propanol (4 ml, 42 mmol), CH₂Cl₂ (200 mL), and triethylamine (11.7 ml, 84 mmol) at room temperature. The reaction solution was concentrated after 45 minutes, and the resulting residue was diluted with EtOAc (40 mL) and washed with brine (30 mL). The organic layer was dried (MgSO₄), filtered, and concentrated to yield a light brown oil. The crude material (2, 8.8 g) was used without further purification.

[0513] Tetrapropylammonium perruthenate (TPAP, 638 mg, 1.8 mmol) was added portion-wise to a solution of 2 (8.6 g, 36.3 mmol), CH₂Cl₂ (73 mL, 2 mL/mmol), 4-methylmorpholine N-oxide (6.4 g, 54.5 mmol), and molecular sieves, 4 Å activated powder (18 g, 500 mg/mmol) at 0° C. under N₂. The reaction was allowed to warm to r.t. after 15 minutes. After 1 hour the reaction was complete (TLC) and was filtered through silica, eluted with EtOAc (100 mL), and the filtrate was concentrated. This yielded 7 g of off-white solid (3). The

material was recrystallized: EtOAc (30 mL), MeOH (10 mL), and Hexanes (1 mL) were added portion wise with heating and sonication. This was brought to a boil after which hexane (100 mL) was added while cooling. Crystals immediately began to precipitate as the solution was cooled. The mixture was filtered and the crystals were washed with hexane (10 mL) to provide 4.88 g (57%) of 3 as off-white fluffy crystals.

Example 16

[0514]



[0515] A mixture of 2-amino-2-methyl-1-propanol (4 ml, 42 mmol), CH₂Cl₂ (200 mL), 4-acetyl benzoic acid (1, 6.9 g, 42 mmol), EDC (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide HCl, 12.1 g, 63 mmol), HOBT (N-hydroxybenzotriazole H₂O, 6.4 g, 42 mmol), and Hunig's base (diisopropylethylamine, 22 mL, 126 mmol) was stirred at room temperature for 18 hours. Upon completion (TLC, LC/MS) the reaction mixture was concentrated, and the resulting residue was diluted with EtOAc (50 mL) and washed with NaHCO₃ (2×40 mL) and brine (40 mL). The organic layer was dried (MgSO₄), filtered, and the filtrate was concentrated. The crude material was purified by flash column chromatography (4:1:1 hexanes:EtOAc:CH₂Cl₂; 1:1:1 hexanes:EtOAc:CH₂Cl₂; 1:1 EtOAc:CH₂Cl₂) to remove bisacylated material. Alcohol 2 was obtained in 54% yield (5.36 g).

[0516] Tetrapropylammonium perruthenate (TPAP, 387 mg, 1.1 mmol) was added portion-wise to a solution of 2 (5.36 g, 22.8 mmol), CH₂Cl₂ (46 mL, 2 mL/mmol), 4-methylmorpholine N-oxide (4 g, 34.2 mmol), and molecular sieves, 4 Å activated powder (11.4 g, 500 mg/mmol) at 0° C. under N₂. The reaction was allowed to warm to r.t. after 15 minutes. After 1 hour the reaction was complete (TLC) and was filtered through silica, which was eluted with EtOAc (100 mL), and the filtrate was concentrated. This yielded 4.4 g of light pink solid (3). The material was recrystallized: 1:1 Hexanes:E-